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(54) **ELECTRODE MATERIAL FOR ELECTROLYTIC HYDROGEN GENERATION**

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(51) **Int. Cl.**
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(Continued)

(52) **U.S. Cl.**
CPC ***C25B 1/04*** (2013.01); ***B01J 23/30*** (2013.01); ***B01J 23/755*** (2013.01);
(Continued)

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CPC B01J 23/30; B01J 23/755; C25B 11/051; C25B 11/065; C01B 32/907
See application file for complete search history.

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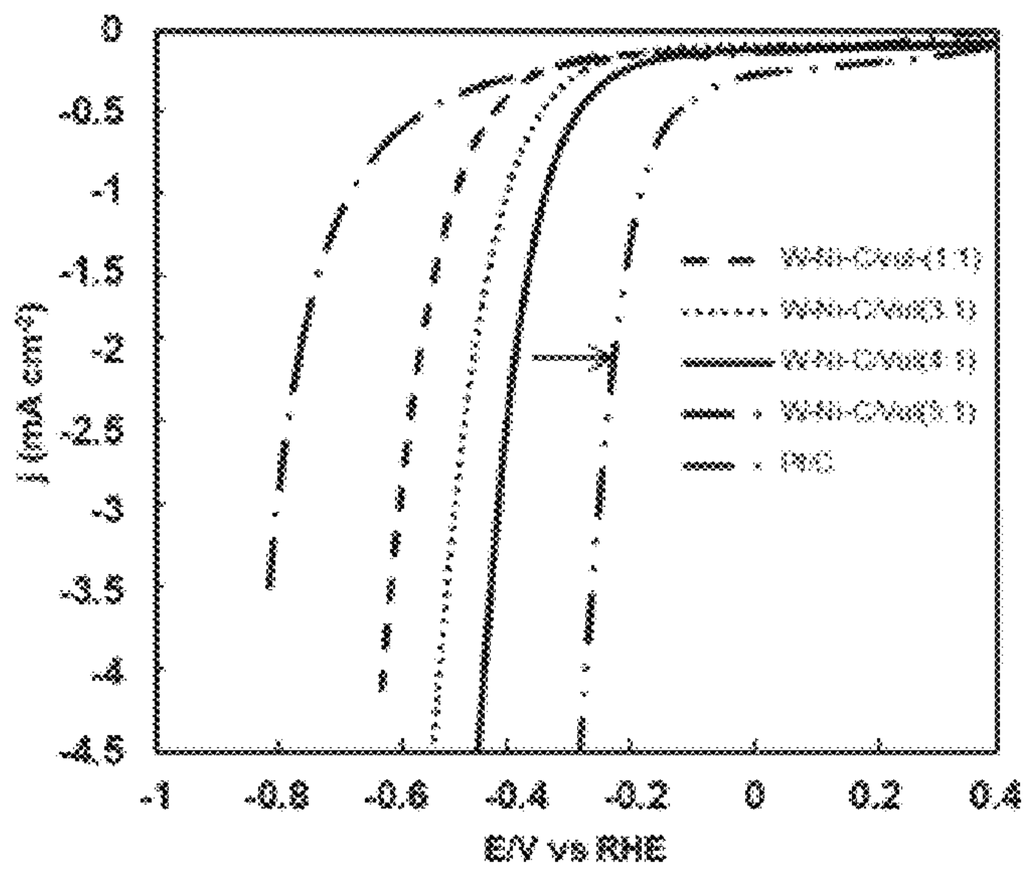
(57) **ABSTRACT**

Some examples of a method for manufacturing an electrode material for electrolytic hydrogen generation are described. Tungsten salt and nickel salt are mixed in a determined molar ratio on a carbon support by effectively controlling synthesis temperature and composition. Water and adsorbed oxygen, produced by mixing the tungsten salt and nickel salt are removed. Then, methane gas is flowed over the mixture resulting in the electrode material. The electrode material is suitable for use as a catalyst in electrolytic hydrogen generation processes, for example, at an industrial scale, to produce large quantities of hydrogen.

18 Claims, 7 Drawing Sheets



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(51) **Int. Cl.**

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B01J 23/30	(2006.01)
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C01B 32/907	(2017.01)

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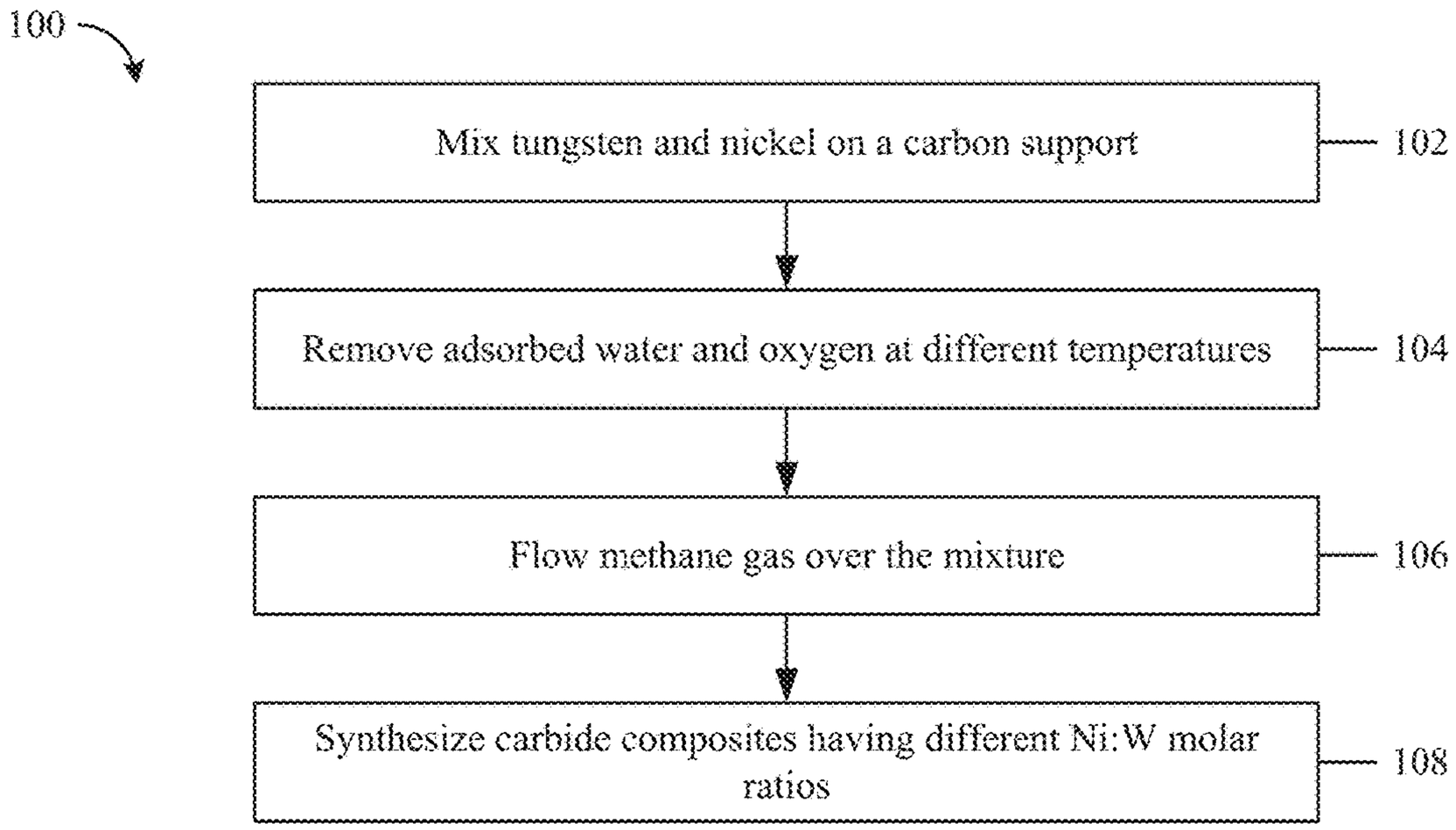

100
Mix tungsten and nickel on a carbon support
102
Remove adsorbed water and oxygen at different temperatures
104
Flow methane gas over the mixture
106
Synthesize carbide composites having different Ni:W molar ratios
108

FIG. 1

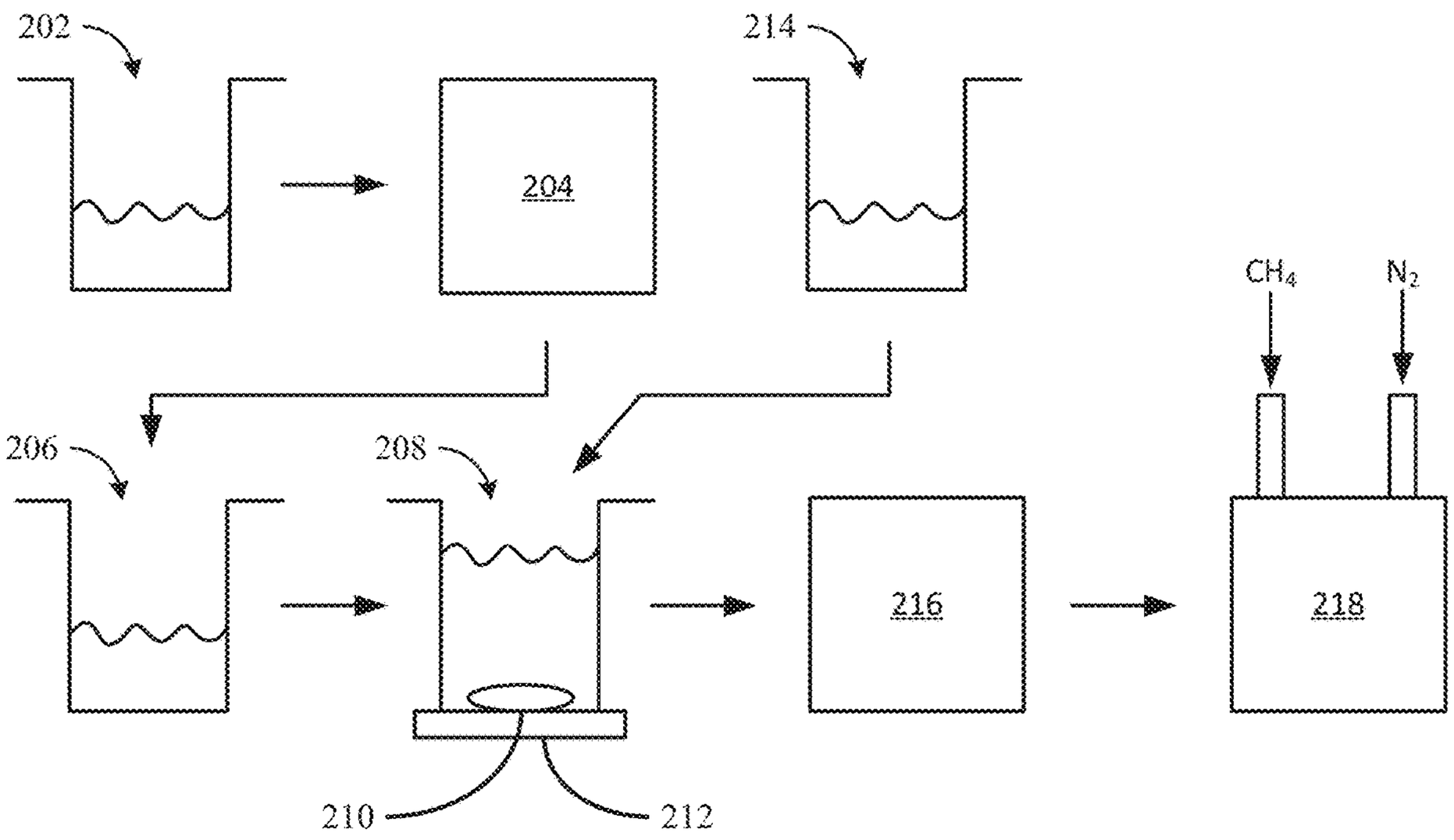

202
214
204
CH4
N2
206
208
216
218
210
212

FIG. 2

FIG. 3A

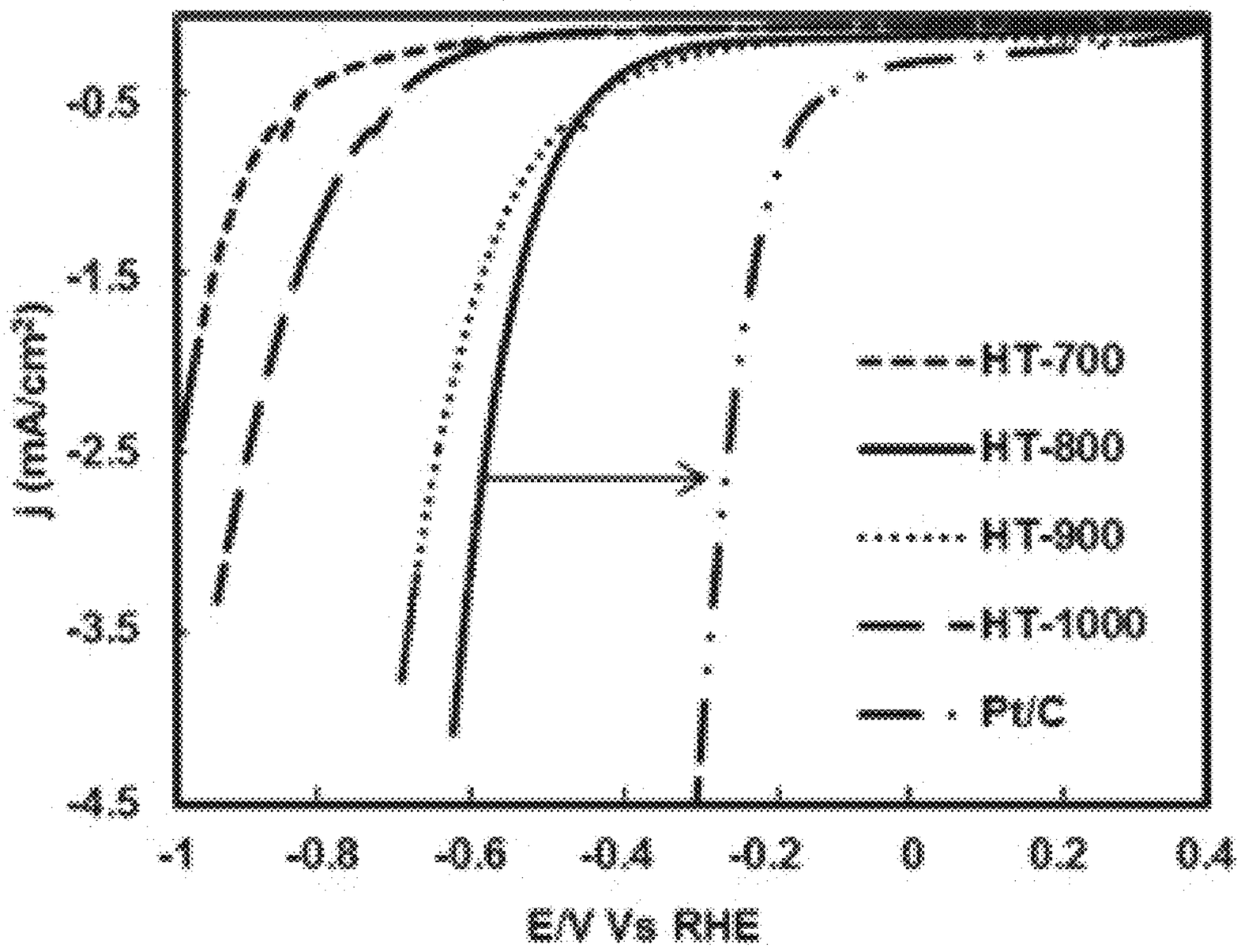

-0.5
-1.5
-2.5
-3.5
-4.5
j (mA/cm²)
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
E/V Vs RHE
HT-700
HT-800
HT-900
HT-1000
Pt/C

FIG. 3B

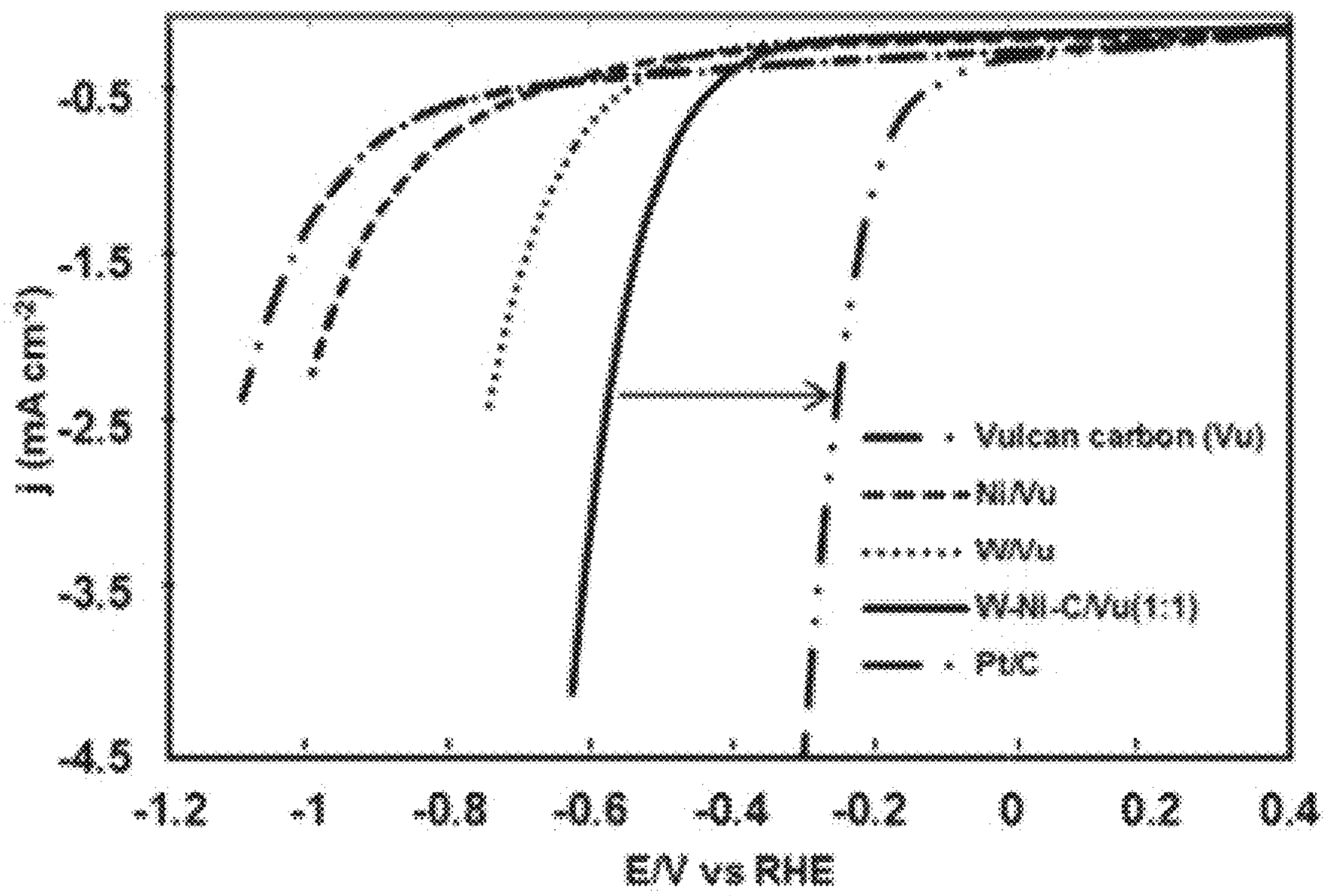

-0.5
-1.5
-2.5
-3.5
-4.5
j (mA cm⁻²)
-1.2
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
E/V vs RHE
Vulcan carbon (Vu)
Ni/Vu
W/Vu
W-Ni-C/Vu(1:1)
Pt/C

FIG. 3C

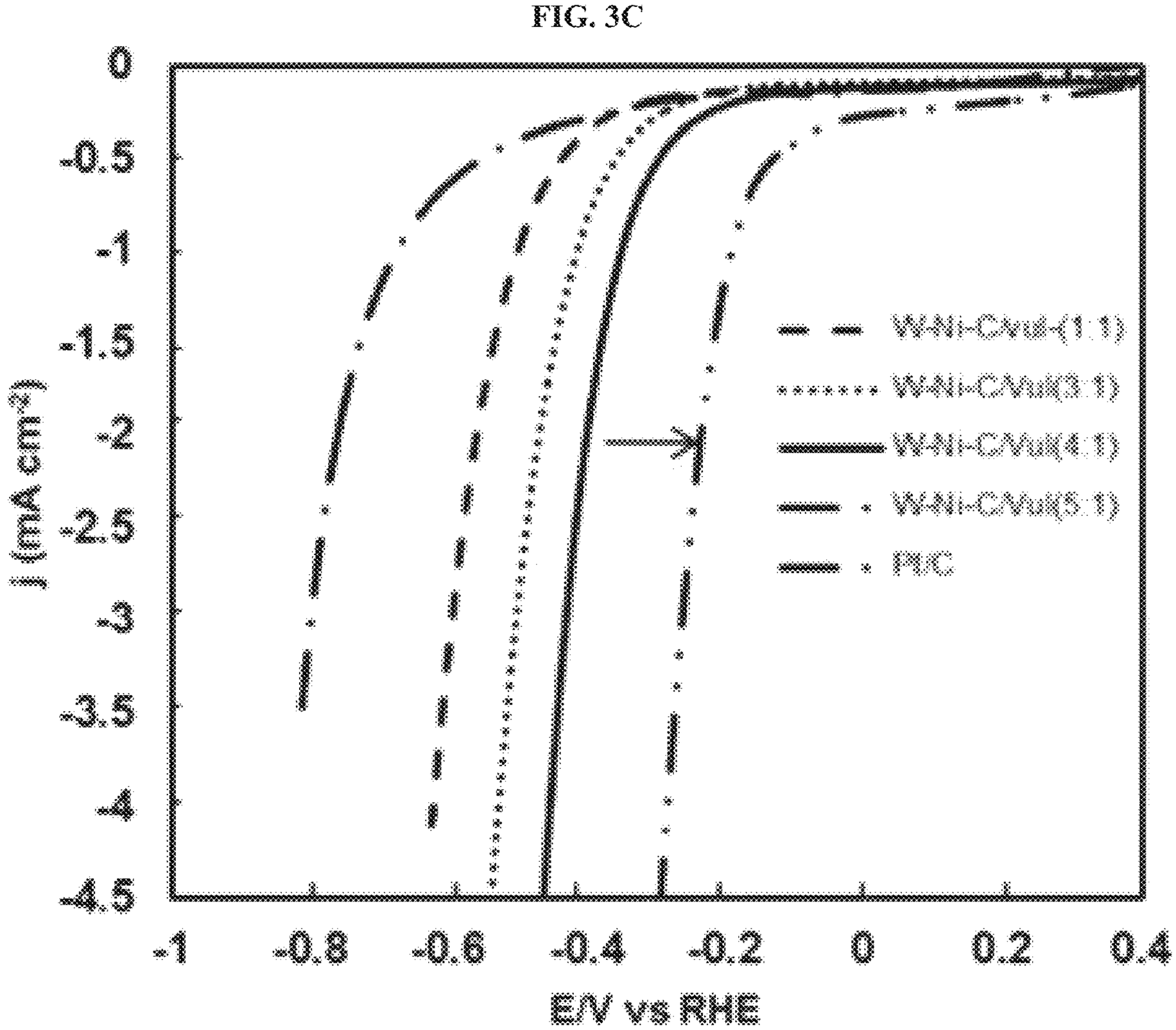

0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
j (mA cm-2)
W-Ni-CMs-(1:1)
W-Ni-CMs(3:1)
W-Ni-CMs(4:1)
W-Ni-CMs(5:1)
Pt/C
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
E/V vs RHE

FIG. 4A

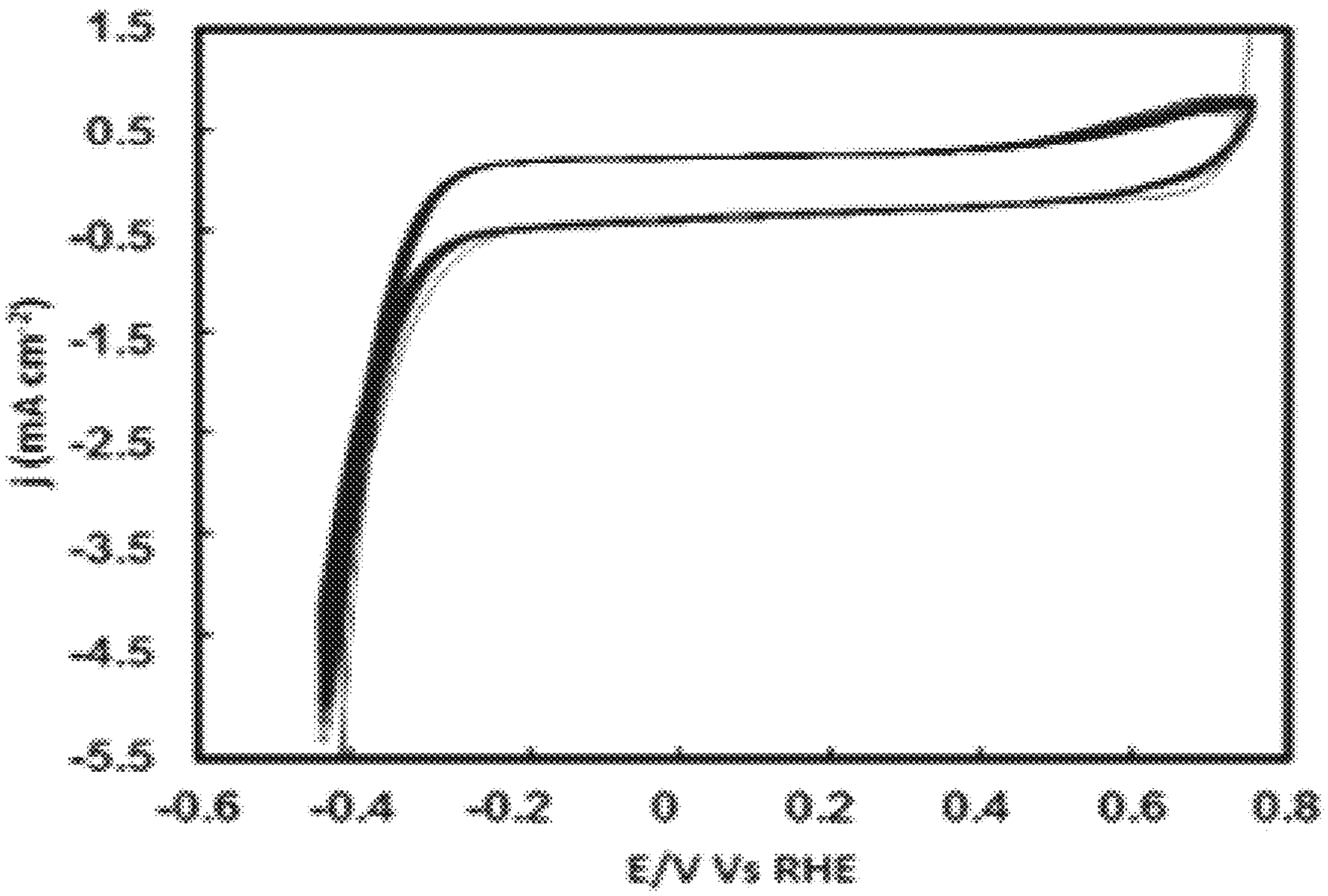

1.5
0.5
-0.5
-1.5
-2.5
-3.5
-4.5
-5.5
j (mA cm⁻²)
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
E/V Vs RHE

FIG. 4B

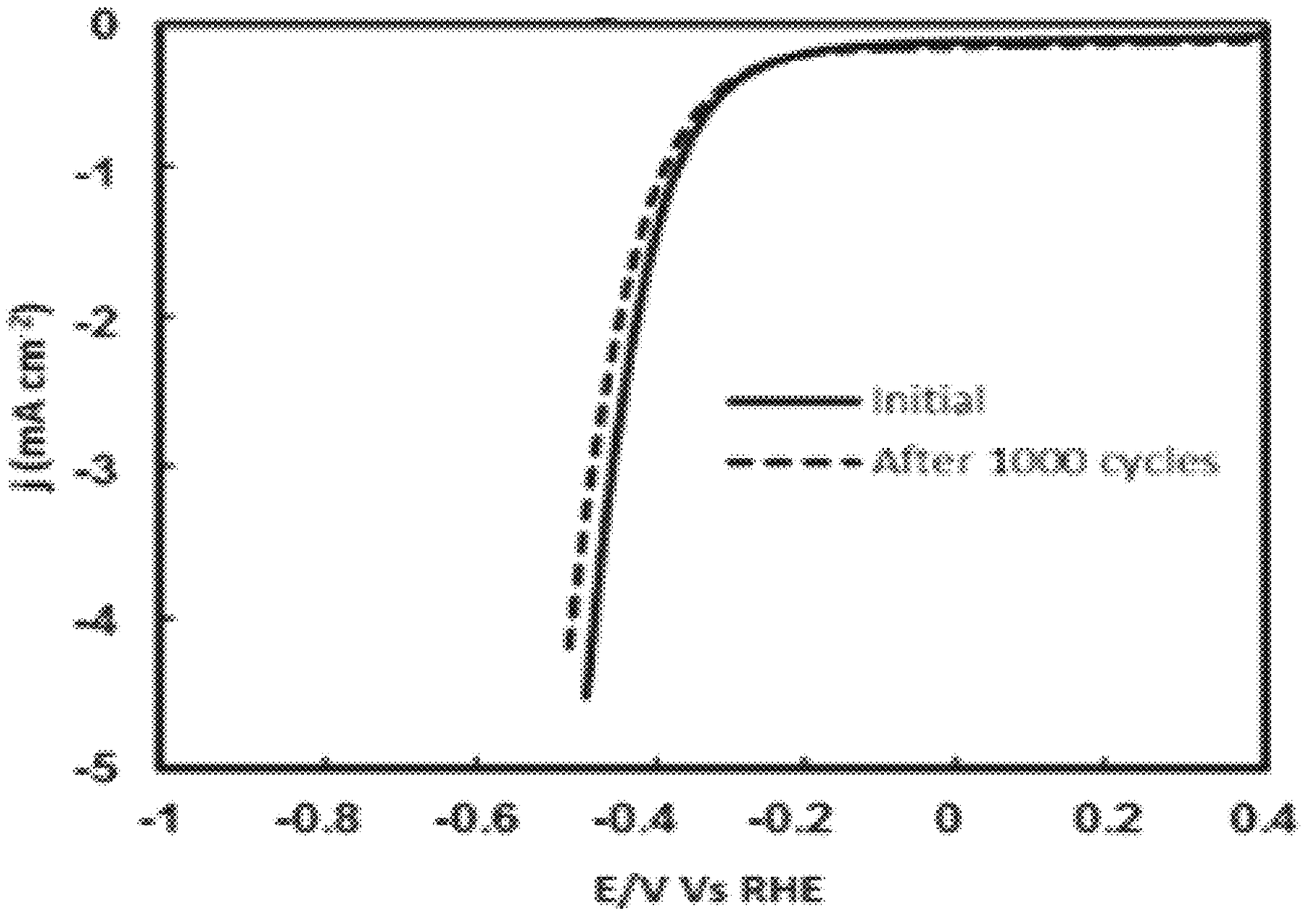
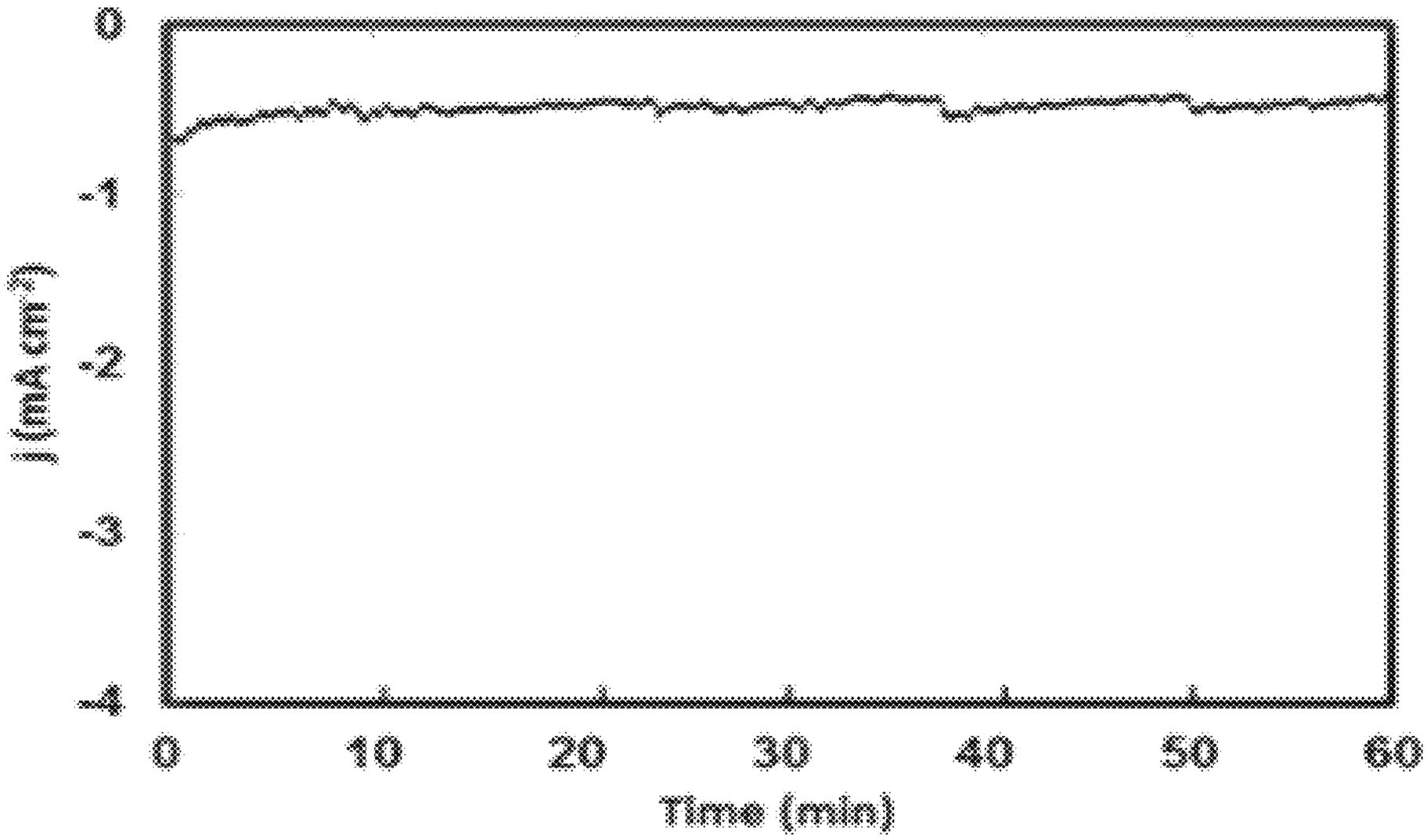

0
-1
-2
-3
-4
-5
j (mA cm⁻²)
Initial
After 1000 cycles
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
E/V Vs RHE

FIG. 4C



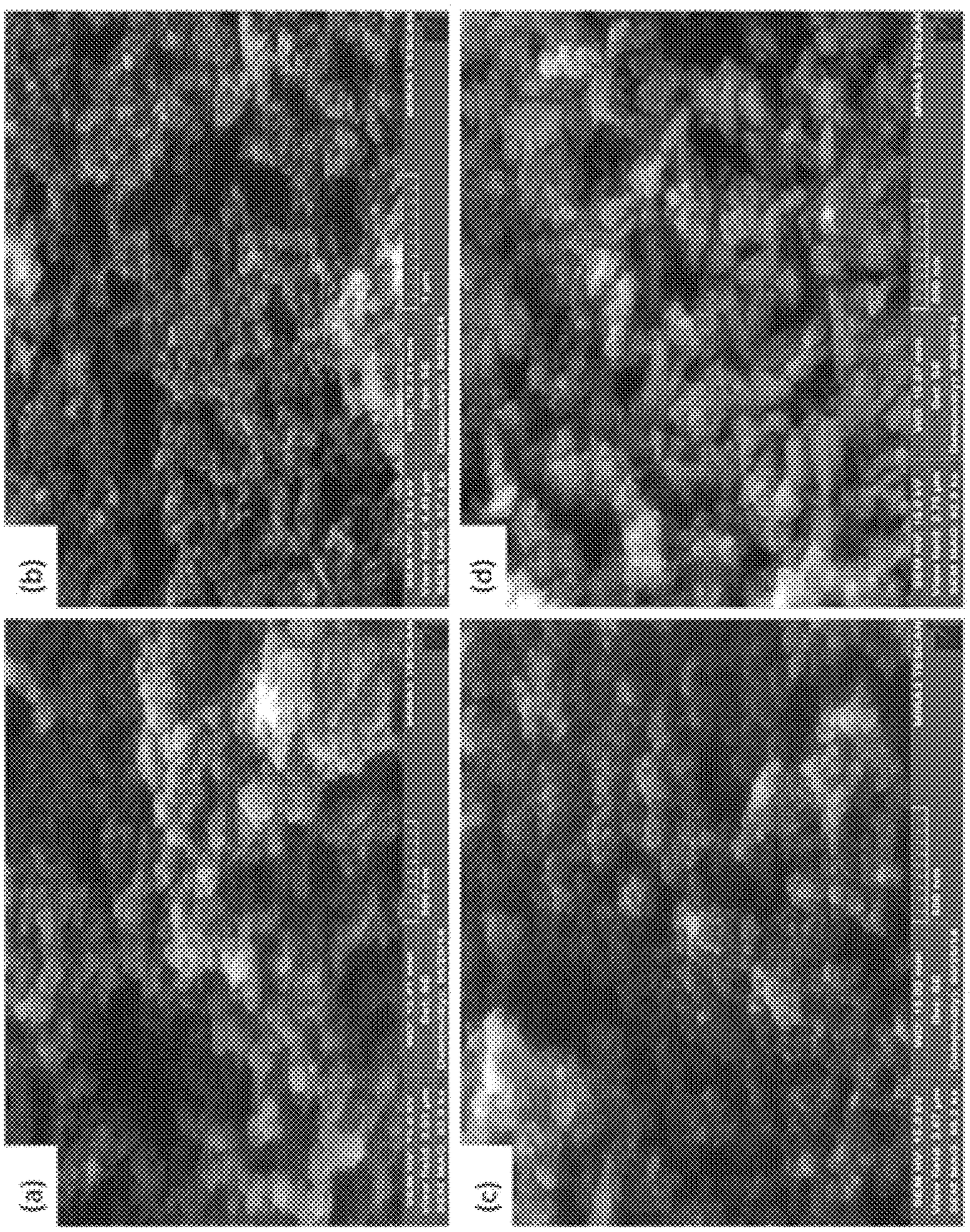


FIG. 5A FIG. 5B FIG. 5C FIG. 5D

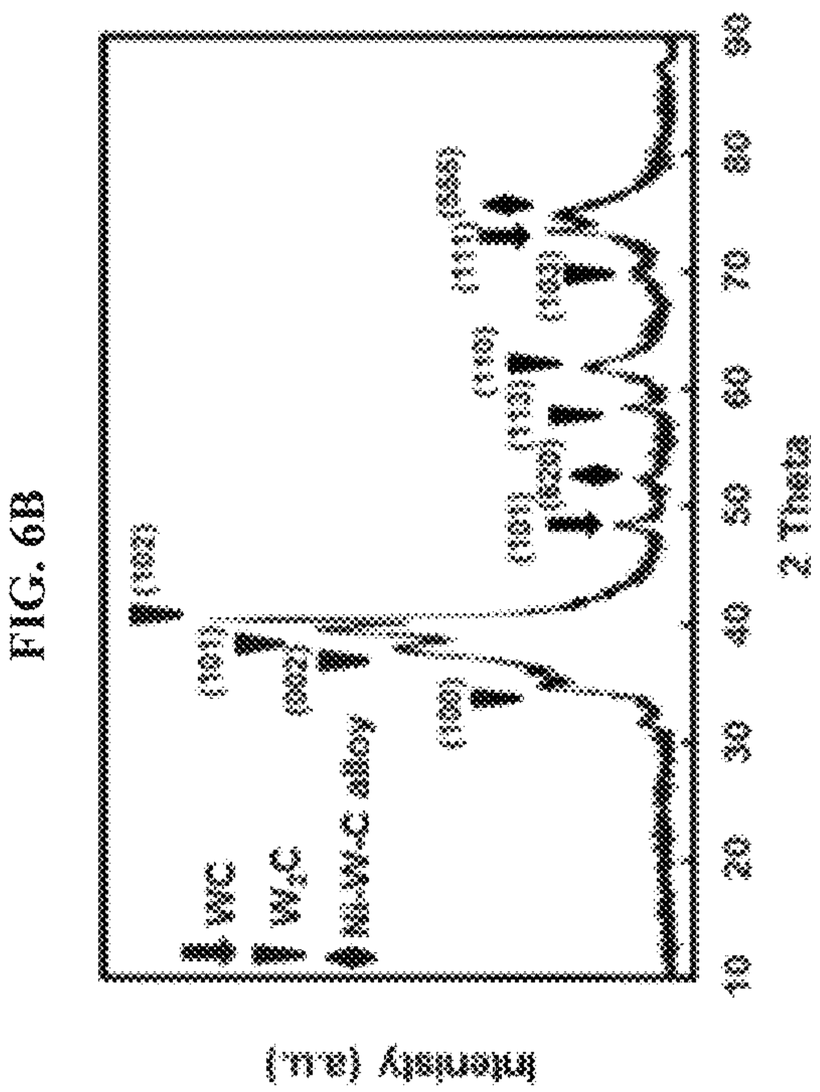


FIG. 6A

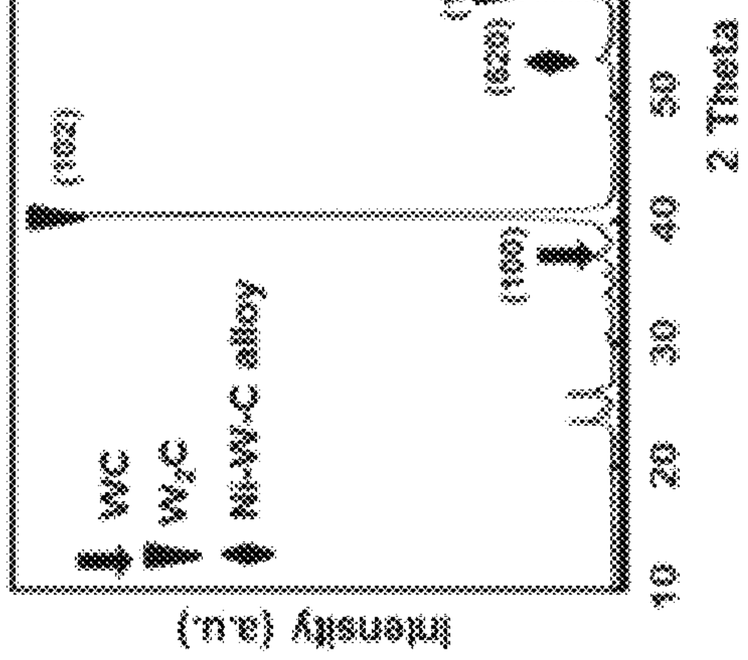


FIG. 6B

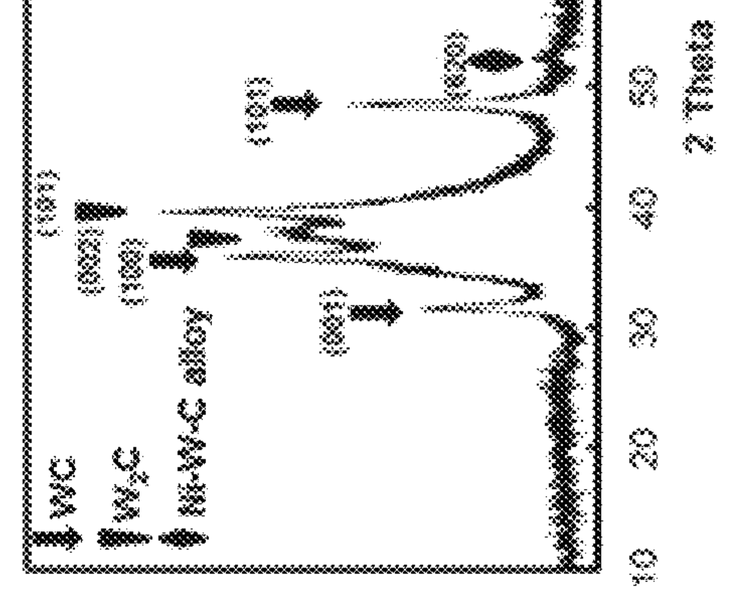


FIG. 6C

FIG. 6D

ELECTRODE MATERIAL FOR ELECTROLYTIC HYDROGEN GENERATION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of and claims the benefit of priority to U.S. patent application Ser. No. 15/147,252, filed May 5, 2016, which claims the benefit of U.S. Provisional Application Ser. No. 62/190,574, filed on Jul. 9, 2015, the contents of which are hereby incorporated by reference.

TECHNICAL FIELD

This disclosure relates to hydrogen generation, for example, by electrolysis.

BACKGROUND

Hydrogen can be produced by several techniques including, for example, steam reforming from hydrocarbons, electrolysis, and thermolysis. Electrolysis of water is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen (H_2) gases due to an electric current being passed through the water. Hydrogen can be produced through photovoltaic/electrolysis systems, alkaline electrolysis, acidic medium electrolysis, methanol oxidation, borohydride solution, or other techniques. Catalysts are often used in electrolytic systems to facilitate hydrogen production. Organic pigments, for example, can be used as catalysts for the release of hydrogen from a hydrogen-rich borohydride solution. Other examples of catalysts include Platinum (Pt). Because industrial quantities of hydrogen can be produced more affordably using hydrocarbons, electrolysis is not frequently used in industrial production of hydrogen.

SUMMARY

This disclosure describes electrolytic hydrogen generation and an electrode material for electrolytic hydrogen generation, for example, from brine water.

Some aspect of the subject matter described here can be implemented as a method. A first quantity of tungsten (W) salt and a second quantity of Nickel (Ni) salt are mixed on a carbon support. Methane gas is flowed over the mixture of the first quantity and the second quantity to form tungsten-nickel carbides (W—Ni—C) on the carbon support. For example, the methane gas is flowed at high temperature. The resulting product was an electrode material suitable for use in electrolytic hydrogen generation, for example, on an industrial scale, to produce large quantities of hydrogen.

This, and other aspects, can include one or more of the following features. The tungsten salt can be dissolved in isopropanol. The nickel salt can be on a carbon support. Water and oxygen can be removed and the methane gas can be flowed over the mixture after removing the water and oxygen. The carbon support can be pre-treated before mixing the first quantity and the second quantity. Pre-treating the carbon support can include removing impurities from the carbon support. Pre-treating the carbon support can include mixing a third quantity of the carbon support with a first volume of hydrochloric acid. The third quantity can include about 0.2 grams (g) of the carbon support. The first volume can include about 40 milliliters (mL). The hydrochloric acid can have a molarity of about 0.5 moles (M). The third quantity can be mixed with the first volume for a duration at a rotational speed. The duration can be about 15 hours. The rotational speed can be about 400 rotations per minute (rpm). Mixing the first quantity of tungsten salt and the second quantity of nickel salt can include selecting the first quantity and the second quantity such that a molar ratio of tungsten salt to nickel salt is about 1:1. The molar ratio of tungsten to nickel can be about 3:1. The first quantity of tungsten salt can consist of WCl_6 and the second quantity of nickel salt can consist of $Ni(NO_3)_2.6H_2O$. The molar ratio of tungsten to nickel can be about 4:1 or 5:1. Mixing the first quantity of tungsten salt and the second quantity of nickel salt on the carbon support can include several steps. A fourth quantity of the carbon support can be dispersed in a second volume of de-ionized water to form a carbon slurry. The first quantity of tungsten salt can be dissolved in a third volume of isopropanol. The dissolved first quantity of tungsten salt in the third volume of isopropanol can be added to the carbon slurry. A fourth volume of de-ionized water can be added to the mixture of the tungsten salt in the carbon slurry. A mixture of the fourth volume of de-ionized water and the mixture of the tungsten salt in the carbon slurry can be stirred for a duration. The mixture of the fourth volume of the de-ionized water and the mixture of the tungsten salt in the carbon slurry can be vacuum dried after the duration. After removing the water and the adsorbed oxygen, flowing the methane gas over the mixture of the first quantity and the second quantity can include increasing a temperature of the mixture to about 1000° C. The temperature can be increased at a rate of about 5 degree Centigrade per minute (° C./min). The temperature of the mixture can be held for a respective duration at each of about 700° C., about 800° C., about 900° C. and about 1000° C. The carbon support can be conductive and hydrophobic. After removing the water and adsorbed oxygen and flowing the methane gas over the mixture of the first quantity and the second quantity, the mixture can be used as an electrode material, for example, as a catalyst, for hydrogen generation from brine by electrolysis. The mixture of the first quantity and the second quantity can be a nickel-tungsten carbide alloy. A surface area of the carbon support can range between about 50 square meters per gram (m^2/g) to about 3000 m^2/g.

Some aspects of the subject matter described here can be implemented as an electrode material for electrolytic hydrogen generation from brine including tungsten-nickel carbide (W—Ni—C) on a carbon support. The tungsten-nickel carbide has a molar ratio of tungsten to nickel of between 1:1 and 5:1.

This, and other aspects, can include one or more of the following features. The molar ratio can be about 1:1, about 2:1, about 3:1, about 4:1 or about 5:1. The carbon support can have a surface area between 50 m^2/g to about 3000 m^2/g. The tungsten-nickel carbides on the carbon supports can have a particle size ranging between about 10 nanometers (nm) and 100 nm. The electrode material can be formed by mixing a first quantity of tungsten (W) salt and a second quantity of nickel (Ni) salt in the presence of a carbon support and flowing methane gas over the mixture of the first quantity and the second quantity to form tungsten-nickel carbides (W—Ni—C) on said carbon support. The first quantity of tungsten salt can consist of WCl_6 and the second quantity of nickel salt can consist of $Ni(NO_3)_2.6H_2O$. The mixture can have water and oxygen removed prior to flowing methane gas over the mixture. The tungsten salt can be dissolved in isopropanol and the nickel salt can be provided on the carbon support. The methane gas flowing over the mixture can increase a temperature of the mixture to about 1000° C.

The details of one or more implementations of the subject matter described in this specification are set forth in the accompanying drawings and the description later. Other features, aspects, and advantages of the subject matter will become apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a flowchart of an example process for producing electrode materials.

FIG. **2** shows a schematic diagram of an example system for producing electrode materials.

FIG. **3**A shows Hydrogen Evolution Reaction (HER) Polarization curves in W—Ni—C/Vu (1:1) at different heat treatment temperature.

FIG. **3**B shows HER Polarization curves in Vulcan carbon (Vu), Ni/Vu, W/Vu, W—Ni—C/Vu (1:1) and Pt/C respectively.

FIG. **3**C shows HER Polarization curves in W—Ni—C/Vu at different mole ratio of Ni:W.

FIG. **4**A shows polarization curves of W—Ni—C/Vu (4:1) in N_2 saturated 0.5 M NaBr, pH~7.04 with consecutive cyclic volt-ammograms recorded, potential scan rate of 50 mV/s.

FIG. **4**B shows polarization curves of W—Ni—C/Vu (4:1) in N_2 saturated 0.5 M NaBr, pH~7.04 before and after 1000 potential sweeps (−0.45 to +0.75 V/RHE), potential scan rate of 20 mV/S.

FIG. **4**C shows chrono-amperometry curves of W—Ni—C/Vu (4:1) in N_2 saturated 0.5 M NaBr, pH~7.04 at −0.37 V/RHE.

FIGS. **5**A-**5**D show Scanning Electron Microscope (SEM) images of electrode materials of different Ni:W molar ratios.

FIGS. **6**A-**6**D show X-Ray diffraction patterns of synthesized catalysts at different mole ratios atomic of Ni to W.

Like reference numbers and designations in the various drawings indicate like elements.

DETAILED DESCRIPTION

Electrolytic or photo-catalytic hydrogen production (or both) from brine water can be an improvement relative to other industrial hydrogen production techniques, for example, in terms of cost and environmental impact. Such hydrogen production techniques use energy that is high enough to dissociate water molecules and release hydrogen. The type of surface on which the dissociation occurs affects significantly the quantity of energy used. Also, energy cost can be affected by using a catalyst that can lower the over voltage of the electrolytic process to produce hydrogen from brine.

Precious metals, for example, platinum (Pt), which are used as catalysts in electrolysis, offer low over potential and faster reaction kinetics for hydrogen evolution reaction (HER). However, such metals, particularly Pt, can be expensive and, consequently, prohibitive for application for hydrogen production from brine on an industrial scale. For example, it is known that coating Pt on Tungsten Carbide (WC), for example, by atomic layer deposition or physical vapor deposition, can reduce Pt loading, but is a complicated process that is difficult to be scaled up to industrial levels.

This disclosure describes electrolytic hydrogen generation and an electrode material for electrolytic hydrogen generation. The electrode material described here can be implemented as an efficient electro-catalyst for hydrogen generation from brine, for example, at industrial levels. As described later, the electrode material is prepared from materials that are abundantly available on earth. The electrode material described here shows significant reduction in over-potential for HER in brine electrolysis. The resulting electrode material can be based on a nano-structured electro-active material and can be implemented as a catalyst in brine electrolysis and can serve as a cost-effective, stable and active alternative to expensive, precious metals, for example, Pt.

In some implementations, the electrode material can include tungsten-nickel based carbides, for example, W_x—Ni_y—C, WC, W_2C, or other tungsten-nickel based carbides, prepared by effectively controlling the synthesis temperature and composition. As described later, such mixtures have shown excellent electro-activeness toward hydrogen evolution reaction from brine with an electrode performance close to that of Pt-based catalysts.

FIG. **1** is a flowchart of an example process **200** for producing electrode materials. In some implementations, the process **100** can be implemented using the system **100**. At **102**, tungsten (W) salt is mixed with nickel (Ni) salt on a carbon support. For example, WCl_6, is mixed with $Ni(NO_3)_2.6H_2O$ on a carbon support, for example, a conductive and hydrophobic carbon support, such as Vulcan XC-72R in a container **102**. In some implementations, a surface area of the carbon support can range between about 50 m^2/g to about 3000 m^2/g. At **104**, water and adsorbed oxygen are removed from the mixture prior to heating at different temperatures, for example, 700° C., 800° C., 900° C., 1000° C. or other temperatures. For example, the mixture resulting by implementing step **102** can be kept in a container **104** having an inert atmosphere, for example, N_2 atmosphere. Then, at **106**, low flow of CH_4 gas, for example, from a CH_4 gas source **106**, can be passed over the mixture to form the carbides at higher temperature, >700° C. For example, the methane gas can be flowed at a low flow rate, for example, 100 milliliters per minute (mL/min) for a reactor of about 5 centimeter (cm) diameter. At **108**, a carbide composite having a specified mole ratio can be synthesized. For example, the mole ratios of Ni to W can be about 1:1, 1:3, 1:4, 1:5 or other mole ratios. In general, the tungsten-nickel carbides can be represented as W_x—Ni_y in carbide form with x being about 50% to 75% atomic and y being about 50% to 25% atomic. In some examples, x can range between 75% and 80%, and y can range between 20% and 25%. In some implementations, the carbide composites can be characterized and also prepared in the form of electrodes, and tested for HER in brine medium using a two or three-electrode electrolytic cell implementation. Experiments described later are performed on a laboratory-scale, but can be scaled up to industrial levels to produce large quantities of the electrode materials.

Experiment I—Pre-Treatment of Carbon Support

FIG. **2** shows a schematic diagram of an example system for producing electrode materials. Initially, Vulcan XC-72R carbon support was pre-treated to remove traces of any impurities, such as metals. In a container **202**, a quantity of 0.2 g of the Vulcan XC-72R was mixed in 40 mL of 0.5 M hydrochloric acid (HCl) for a duration of approximately 15 hrs at moderate temperature (20° C.-40° C.), while stirring at 400 rpm, for example, using a magnetic stirrer. The quantity of carbon support, for example, Vulcan XC-72R, ranged from 0.3 g to 0.4 g during pre-treatment in acid. In general, a quantity of carbon support used can depend on an amount of electrode material, for example, catalyst, to be produced. After carbon cleaning, for example, by the pre-

treatment described here, in acid to remove traces of impurities, for example, metals or other impurities, 0.2 g of treated carbon was used to develop the carbide materials on the carbon surface. The amount of carbon used can be more than the amount of carbon needed to account for carbon loss. The carbon support was then filtered, washed and dried in an oven **204** at 80° C. for 6-7 hrs.

Experiment II—Preparation of Electrode Material Having Ni:W in a 1:1 Ratio

To prepare the electrode material, 0.2 g of Vulcan carbon, pre-treated as described earlier, was dispersed in a container **206** containing 40 mL de-ionized water by sonication for 20-30 minutes, and then transferred to a glass beaker **208** with magnetic stirrer **210** (rotated by a stir plate **212**) to form a carbon slurry. Thereafter, 0.4 g of WCl_6 dissolved in a container **212** containing 30 mL isopropanol (IPA) was slowly added to the carbon slurry. To maintain an atomic ratio of Ni:W or 1:1, 0.29 g of $Ni(NO_3)_2.6H_2O$ was dissolved in a container **214** containing 20 mL of de-ionized H_2O and added, drop-wise, to the mixture in the container **208**, followed by a final rinse with 10 mL of de-ionized H_2O to make-up 100 mL of reaction volume. The mixture was left under stirring at 500 rpm for 2-3 days for proper impregnation of metal salts onto the carbon matrix. The mixture was then vacuum-dried at 80° C. between 6 and 7 hrs in an oven **216**.

The resulting sample was heat-treated as follows. The powdered sample was placed in a crucible boat and transferred into a quartz tube MTI furnace 218 (OTF-1200X-S). Gas cylinders were connected to the gas inlet of the furnace and the exhaust/outlet was directed to an oil bath. Nitrogen (N_2) gas was first passed into the furnace while the temperature was first increased from room temperature to 100° C. for 30 minutes and held at this temperature for 10 minutes to purge out adsorbed oxygen and water. Methane (CH_4) gas flow was then passed while ramping temperature of the furnace at a rate of 5° C./min to the desired temperatures of 700° C., 800° C., 900° C. or 1000° C., and held for 1 hr. In general, a quality of the sample is affected by a ramping period, that is, the time to reach a set temperature value at which catalyst formation begins and a temperature hold period, that is, the time for which the temperature is held for catalyst active sites formation.

Subsequently, some of the samples synthesized at Ni:W ratio of 1:1 were cooled and used to study the effect of temperature on HER performance, as described later. In some implementations, the samples can be cooled at any rate. For example, the cooling can be done under ambient conditions without an external cooling system. In some implementations, external cooling systems can be used to cool the samples at cooling rates ranging between about 5° C./min and 10° C./min. In some implementations, the cooling can be implemented by simply turning off the heating chamber in which the samples are heated. Cooling can be done under the flow of methane or an inert gas to avoid leak of oxygen into reactor.

Experiment III-V—Preparation of Electrode Material Having Ni:W in a 1:3, 1:4 and 1:5 Ratio, Respectively

To prepare the electrode material having Ni:W in ratios of 1:3, 1:4 and 1:5, 1.2 g, 1.6 g and 2.0 g of WCl_6, respectively, was mixed with 0.29 g of Vulcan carbon, pre-treated as described earlier. The electrode material in each of these ratios was prepared by processing each mixture in a manner similar to that described earlier. Each obtained sample was characterized using a thin film electrode in a three-electrode geometric cell and also by spectroscopic techniques to investigate the morphological structure and composition of each sample.

For each sample prepared as described later, HER activity in brine were studied, as described later.

Experiment VI—Studying HER Activity in Brine

For each sample prepared as described earlier, approximately 5 mg of the sample was dispersed in a mixture of water and isopropanol (30% V/V) and 37 μL of 1.66% wt Nafion® (prepared from 5% wt). The mixture was sonicated to obtain a uniform ink. The working electrode used during electrolysis was prepared by depositing 16 μL of the ink suspension on the pre-cleaned glassy carbon substrate and allowed to dry under air flow at room temperature. The loading operation was repeated until the desired catalyst loading, 0.4 mg/cm^2 was achieved and the geometric area of the glassy carbon rotating disk electrode (RDE) was about 0.196 cm^2. A Pt mesh was used as a counter electrode during activity measurements in brine (0.5 M NaBr, pH~7.04, specific gravity~1.54). A Calomel electrode (calibrated against reversible hydrogen electrode every day prior to activity measurement of HER) was used as a reference electrode. All potential measurements during these studies were converted to reversible hydrogen electrode (RHE).

Results—HER Activity in Brine

FIG. **3**A shows HER polarization curves for Ni:W in a mole ratio of 1:1 at different heat treatment temperatures in the presence of methane gas flow. The polarization curves show that sample treated at 800° C. shows better HER activity than the other samples with an over-voltage of 300 millivolt (mV) as compared to Pt/C catalyst. This can indicate that formation of more active sites for HER for the specific composite is more favorable at this temperature.

FIG. **3**B shows HER polarization curves obtained for individual metal carbides. Vulcan carbon shows the highest over potential for HER. WC/Vu behaves better than its homologue, NiC/C. A significant improvement in HER activity is observed when both metals are incorporated at 1:1 mole ratio of Ni:W.

FIG. **3**C shows HER polarization curves in brine for the carbide composites including two metals. The polarization curves were generated to study if the electro-catalytic synergistic effect of the two metals increased the HER performance of the carbide composite. An increase in current density and a reduction in over-potential were observed with HER activity close to that of bulk Pt/C. When the mole ratio of Ni:W was optimized from 1:1 to 1:4, a corresponding reduction in over potential was significant. However, when the ratio is 1:5, a drastic reduction in activity of the catalyst toward HER in brine was noticed suggesting that the best molar ratio of Ni:W to lead to metal carbide alloys as potential Pt-free electro-catalyst for HER is 1:4. Such enhancement in HER activity may be due to effective utilization of the synergistic effect of the two metals that favor faster HER kinetics.

Experiment and Results—Catalyst Stability

For stability studies, the catalyst that demonstrated highest HER activity, that is, Ni:W in a molar ratio of 1:4 (for example, W—Ni—C/Vu in a 4:1 ratio), was used. To investigate the long term performance for the catalyst in brine, potential sweeps were conducted from −0.45 to +0.75V/RHE for 1000 cycles as shown in FIG. **4**A. FIG. **4**B shows the polarization curve recorded before and after the stability test. The catalyst demonstrated good stability by maintaining almost its initial polarization behavior in brine medium. To further establish the catalyst stability, chrono-

amperometry (CA) studies was also conducted at a potential hold of −0.37 V/RHE (corresponding to j=1 mA cm^{-2}) for 1 hr as shown in FIG. **4**C.

Scanning Electron Microscope (SEM) Images and X-Ray Diffraction

FIGS. **5**A-**5**D are Scanning Electron Microscope (SEM) images of electrode materials of different Ni:W molar ratios. FIG. **5**A is the SEM image of the composition having W:Ni in a 1:1 ratio. FIG. **5**B is the SEM image of the composition having W:Ni in a 3:1 ratio. FIG. **5**C is the SEM image of the composition having W:Ni in a 4:1 ratio. FIG. **5**D is the SEM image of the composition having W:Ni in a 5:1 ratio. The composite with molar ratio of W:Ni of 5 to 1 (FIG. **5**D) appears to be more dense than those corresponding to ratios, 4:1, 3:1, and 1:1. The difference in density may be the reason that HER activity was decreased significantly for this composition relative to the other compositions.

FIGS. **6**A-**6**D show X-Ray diffraction patterns of synthesized catalysts at different mole ratios atomic of Ni to W. FIG. **6**A is an XRD pattern of catalyst having W:Ni in a 1:1 ratio. FIG. **6**B is an XRD pattern of catalyst having W:Ni in a 3:1 ratio. FIG. **6**C is an XRD pattern of catalyst having W:Ni in a 4:1 ratio. FIG. **6**A is an XRD pattern of catalyst having W:Ni in a 5:1 ratio. The XRD patterns of the synthesized catalysts show formations of mixture of metal carbides of tungsten metal (WC and W_2C) and W—Ni carbides alloys at different diffraction angles. The unassigned peak in the XRD figure corresponds to Carbon (002) plane.

In summary, the electrode material described here can serve as a cost effective and cheaper alloy material that can be used for hydrogen formation from brine through electrolysis. The alloy composition described here can allow hydrogen formation at high rates. The alloy composition can replace relatively more expensive, precious metals, for example, Pt.

Thus, particular implementations of the subject matter have been described. Other implementations are within the scope of the following claims.

The invention claimed is:

1. A method for forming an electrode for brine electrolysis comprising:

mixing a tungsten (W) salt with a nickel (Ni) salt on a carbon support to give a mixture;

removing adsorbed oxygen from the mixture;

flowing methane gas over the mixture and increasing temperature of the mixture after removing adsorbed oxygen to form tungsten-nickel carbides (W—Ni—C) on the carbon support, wherein the molar ratio of tungsten to nickel is about 4:1;

forming an ink suspension from the mixture on the carbon support by dispersing the mixture in a water based solvent;

depositing the ink suspension on a glassy carbon substrate; and

drying the ink suspension on the glassy carbon substrate to form the electrode.

2. The method of claim **1**, comprising dissolving the tungsten salt in isopropanol.

3. The method of claim **2**, wherein the nickel salt is disposed on the carbon support, and wherein mixing the tungsten salt with the nickel salt comprises mixing the tungsten salt dissolved in the isopropanol with the nickel salt as disposed on the carbon support.

4. The method of claim **1**, wherein mixing the tungsten (W) salt with the nickel salt (Ni) on the carbon support comprises:

dissolving the tungsten salt in isopropanol;

dispersing the nickel salt as disposed on the carbon support in water to form a carbon slurry;

mixing the tungsten salt dissolved in the isopropanol with the carbon slurry; and

vacuum drying to give the mixture.

5. The method of claim **1**, wherein increasing the temperature comprises increasing temperature of the mixture at a rate of at least 5° C. per minute.

6. The method of claim **1**, wherein increasing temperature comprises increasing temperature of the mixture to at least 1000° C.

7. The method of claim **6**, wherein increasing temperature comprises holding temperature of the mixture at less than 1000° C. for a duration.

8. The method of claim **1**, comprising pre-treating the carbon support to remove impurities from the carbon support before mixing the tungsten salt with the nickel salt.

9. The method of claim **8**, wherein pre-treating the carbon support comprises mixing the carbon support with an acid to form a slurry of the carbon support in the acid, and filtering the carbon support from the slurry.

10. The method of claim **9**, wherein the acid comprises hydrochloric acid.

11. The method claim **1**, wherein the tungsten salt comprises WCl_6 and the nickel salt comprises $Ni(NO_3)_2$ $6H_2O$.

12. The method of claim **1**, wherein the carbon support is conductive and hydrophobic, wherein a surface area of the carbon support is in a range of about 50 square meters per gram (m^2/g) to about 3000 m^2/g, and wherein the tungsten-nickel carbides on the carbon support have a particle size ranging between about 10 nanometers (nm) and 100 nm.

13. The method of claim **1**, wherein flowing methane over the mixture comprises flowing methane through the mixture producing the tungsten-nickel carbides as a nickel-tungsten carbide alloy.

14. The method of claim **1**, comprising generating hydrogen from brine by electrolysis of the brine via electrode material, wherein the electrode material comprises the tungsten-nickel carbides on the carbon support.

15. A method of electrolytic hydrogen generation, comprising generating hydrogen from brine by electrolysis of the brine via an electrode comprising an electrode material, wherein the electrode material comprises a tungsten-nickel carbide on a carbon support, wherein the molar ratio of tungsten to nickel is about 4:1, wherein the electrode is formed by:

dispersing the electrode material in a water based solvent to form an ink suspension;

depositing the ink suspension on a glassy carbon substrate; and

drying the ink suspension on the glassy carbon substrate to form the electrode.

16. The method of claim **15**, wherein the tungsten-nickel carbide comprises a tungsten-nickel carbide alloy.

17. The method of claim **15**, wherein the tungsten-nickel carbide on the carbon support has a particle size in a range of 10 nanometers (nm) to 100 nm, wherein the carbon support is conductive and hydrophobic, and wherein the carbon support comprises a surface area in a range of 50 square meters per gram (m^2/g) to 3000 m^2/g.

18. The method of claim **15**, wherein the tungsten-nickel carbide on the carbon support is formed by removing adsorbed oxygen from a mixture of a tungsten salt and a nickel salt on the carbon support and subsequently flowing methane over the mixture.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 11,384,439 B2
APPLICATION NO. : 16/535914
DATED : July 12, 2022
INVENTOR(S) : Merzougui et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims

Column 8, Line 25 (approx.), Claim 11, after "method" insert -- of --;

Column 8, Line 26 (approx.), Claim 11, delete "$Ni(NO_3)_2$ $6H_2O$." and insert -- $Ni(NO_3)_2 \cdot 6H_2O$. --.

Signed and Sealed this
Thirtieth Day of May, 2023

Katherine Kelly Vidal

Katherine Kelly Vidal
Director of the United States Patent and Trademark Office